

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 March 2002 (14.03.2002)

PCT

(10) International Publication Number
WO 02/20708 A1

(51) International Patent Classification⁷: **C11D 3/37**

(US). **CHIOU, Yu-Min, Catherine**; Unilever Research U.S. Inc., 45 River Road, Edgewater, NJ 07020 (US).

(21) International Application Number: **PCT/EP01/09274**

(22) International Filing Date: **9 August 2001 (09.08.2001)**

(74) Agents: **TANSLEY, Sally, Elizabeth et al.**; Unilever PLC, Patent Department, Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
09/658,175 **8 September 2000 (08.09.2000)** **US**

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(71) Applicant (*for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, SD, SG, SL, SZ, TT, TZ, UG, ZA, ZW only*): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for AL, AM, AT, AZ, BA, BE, BG, BR, BY, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GE, GR, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, MX, MZ, NL, NO, PL, PT, RO, RU, SE, SI, SK, TJ, TM, TR, UA, UZ, VN, YU only*): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

(71) Applicant (*for IN only*): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, 400 020 Mumbai, Maharashtra (IN).

(72) Inventors: **GHATLIA, Naresh, Dhirajlal**; Unilever Research U.S. Inc., 45 River Road, Edgewater, NJ 07020

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **POLYCARBOXYLIC ACID CONTAINING THREE-IN-ONE DISHWASHING COMPOSITION**

(57) Abstract: A dishwashing composition with hydrophobically modified polycarboxylic acids and water-soluble entities that reduce phosphate scale formation is described. The dishwashing composition displays excellent cleaning benefits and glass appearance, even in the absence of NaCl additives and conventional rinse aid compositions.

- 1 -

POLYCARBOXYLIC ACID CONTAINING
THREE-IN-ONE DISHWASHING COMPOSITION

5

Field of the Invention

This invention is directed to a composition for use in
10 a dishwashing machine. More particularly, the invention is
directed to a superior dishwashing composition that has a
hydrophobically modified polycarboxylic acid and a water
soluble polymer that reduces phosphate scale formation. The
dishwashing composition unexpectedly results in excellent
15 cleaning properties and excellent glass appearance when used
to clean glassware even in the presence of hard water and in
the absence of conventional rinse aid compositions.

20

Background of the Invention

Dishwashing compositions constitute a generally
recognised distinct class of detergent compositions,
particularly when compared to detergents designed for fabric
25 washing. For example, the ultimate dishwashing composition
results in a spotless and film-free appearance on glassware
and silverware after a cleaning cycle in a dishwashing
machine. In fabric washing operations, on the otherhand,
detergent compositions which result in greasy, oily or soapy
30 residues on items that were cleaned can be tolerated.

Often, washing articles in a commercially available
dishwashing machine entails using three products. Salt is

- 2 -

added to the salt compartment to recharge the ion exchanger which softens the water, a dishwashing formulation is used to clean the articles and a rinse aid is used to ensure that the articles are rinsed with no streaks or smears.

- 5 Consumers generally find it very inconvenient, however, to replace or refill such products.

In order to provide convenient products to consumers, manufacturers have been making dishwashing tablets in order
10 to eliminate detergent handling and dosing issues. Such tablets often have a detergent portion, and a wax portion which contains a rinse aid. These types of tablets, which are sometimes referred to as 2-in-1 tablets, have disadvantages since they may only be used in a wash cycle
15 that does not exceed 55°C. This is true because the wax portion which contains the rinse aid will completely dissolve in a wash cycle that exceeds 55°C. This causes all of the rinse aid to drain out of the dishwashing machine before the actual rinse cycle. Furthermore, such 2-in-1
20 tablets require that salt be added to the dishwashing machine in order to obtain optimal results, and they are very complicated and expensive to produce.

Other types of tablets that are well known are often
25 referred to as pH sensitive 2-in-1 tablets. These types of tablets have a detergent portion and rinse aid portion that is contained in a pH sensitive material. The pH sensitive 2-in-1 tablets may be used in wash cycles that exceed 55°C. However, like the detergent tablets with the wax portion,
30 the pH sensitive 2-in-1 tablets require that salt be added to the dishwashing machine in order to obtain optimal

- 3 -

cleaning results and they are extremely expensive to produce.

In view of the vast deficiencies of the conventional products, it is of increasing interest to provide a dishwashing composition, such as a dishwashing tablet, that works well at all wash temperatures of a dishwashing system (even temperatures greater than 55°C), provides antiscaling benefits in a system that is high in phosphate content (in hard water), does result in excellent cleaning benefits in water that has not been subjected to conventional water softening additives (i.e., hard water) and provides a glossy glassware appearance in the absence of conventional rinse aid compositions. This invention, therefore, is directed to a dishwashing composition that has a hydrophobically modified polycarboxylic acid and a water soluble polymer that reduces phosphate scale formation on glassware being cleaned. The dishwashing composition is superior in that it unexpectedly results in excellent cleaning properties, and reduced spotting and scale formation even when no salt is added to the dishwashing machine to soften hard water, when washing cycles exceed a temperature of 55°C, and when no rinse aid composition is added to the dishwashing machine. In fact, the present invention is directed to a superior 3-in-1 detergent composition that is inexpensive to produce and very easy for the consumer to use.

Background Material

Efforts have been made to prepare dishwashing compositions. In U.S. Patent No. 5,939,373, an automatic

- 4 -

dishwashing detergent composition comprising a phosphate builder and a metal containing bleach catalyst is described.

Still other efforts have been disclosed for making dishwashing compositions. In WO 00/06688, a dishwashing composition with a coated core is described. The coated core has a substance that exerts function in a clear rinse cycle.

Even further, other efforts have been disclosed for making dishwashing compositions. In DE 197 27 073 A1, coated detergent components are described.

None of the material above describes a dishwashing composition that has a hydrophobically modified polycarboxylic acid and a water soluble polymer that reduces phosphate scale formation wherein the dishwashing composition results in excellent cleaning properties and glass appearance when used, for example, in the presence of hard water, in the absence of rinse aid compositions and even in a washing cycle that exceeds a temperature of 55°C.

Summary of the Invention

In a first aspect, the present invention is directed to a hard water dishwashing composition effective for cleaning and reducing spotting and phosphate scale formation on glassware, the dishwashing composition comprising:

a) a hydrophobically modified polycarboxylic acid; and

- 5 -

- b) a water soluble polymer that reduces phosphate scale formation.

5 In a second aspect, this invention is directed to a method for minimizing spotting and phosphate scale formation on glassware being cleaned, comprising the steps of:

- 10 a) subjecting the glassware to a dishwashing composition comprising a hydrophobically modified polycarboxylic acid, and a water soluble polymer that reduces phosphate scale formation;
- b) subjecting the glassware to hard water; and
- c) removing the glassware from the hard water

15 wherein the glassware is not subjected to a rinse aid composition.

20 In a third aspect, this invention is directed to a package comprising the dishwashing composition described in the first aspect of this invention and instructions not to use a rinse aid composition or conventional water softening salts or both.

25 As used herein, glassware is defined to include drinking glasses and any other articles typically found in a commercial or domestic dishwasher.

30

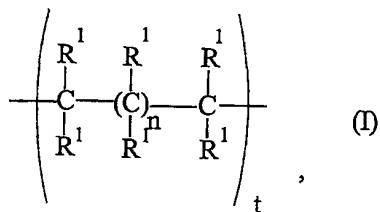
- 6 -

Detailed Description of the Preferred Embodiments

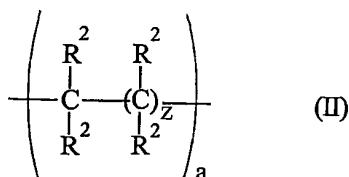
As used in this invention, a hydrophobically modified
5 polycarboxylic acid is defined to mean a compound, oligomer
or polymer having at least one carboxylic acid group and at
least one group that is not water soluble. There generally
is no limitation with respect to the type of hydrophobically
modified polycarboxylic acid that may be used in this
10 invention other than that the polycarbocyclic acid can be
used in a dishwashing composition that comprises a water
soluble polymer that reduces phosphate scale formation.
Such a hydrophobically modified polycarboxylic acid often
has a weight average molecular weight of greater than about
15 175 and less than about 1.5 million, and preferably, greater
than about 200 and less than about 1 million; and most
preferably, greater than about 225 and less than about 750
thousand, including all ranges subsumed therein.

- 7 -

The preferred hydrophobically modified polycarboxylic acid which may be used in this invention comprises at least one structural unit of the formula:



and



wherein each R^1 and R^2 are independently a hydrogen, hydroxy, alkoxy, carboxylic acid group, carboxylic acid salt, ester group, amide group, aryl, C_{1-20} alkyl, C_{2-20} alkenyl, C_{2-20} alkynyl or a polyoxyalkylene condensate of an aliphatic group, n is an integer from about 0 to 8, z is an integer from about 1 to about 8, t is an integer from about 0 to about 2,000 and a is an integer from about 0 to about 2,000, with the proviso that a and t are not simultaneously 0 and at least one R^1 or one R^2 is a carboxylic acid group, or a salt thereof.

In a preferred embodiment, the hydrophobically modified polycarboxylic acid used in this invention comprises at least one structural unit represented by formula I ($t \geq 1$) with at least one R^1 as a carboxylic acid group (or salt

- 8 -

thereof), and at least one structural unit represented by formula II ($a \geq 1$) with at least one R^2 group as a C_{4-20} alkyl group or a C_{8-30} ethoxylated condensate of an aliphatic group.

5 In a most preferred embodiment, however, the modified polycarboxylic acid used in this invention comprises structural units represented by formula I and structural units represented by formula II wherein a is from about 80% to about 120% of t , and at least two R^1 groups are carboxylic
10 acid groups (or salts thereof) and at least one R^2 group is a methyl group and at least one R^2 group is a C_5 alkyl, and n is 0 and z is 1.

The hydrophobically modified polycarboxylic acids which
15 may be used in this invention are typically prepared by reacting the desired precursors (sp^2 bonded monomers) under free radical polymerization conditions. Such polycarboxylic acids are also commercially available from suppliers like Rohm & Haas and DuPont. A more detailed
20 description of the types of hydrophobically modified polycarboxylic acids which may be used in this invention, including the process for making the same, may be found in U.S. Patent No. 5,232,622, the disclosure of which is incorporated herein by reference.

25

The preferred and most preferred hydrophobically modified polycarboxylic acids are made available by Rohm & Haas under the names Acusol 820 and 460, respectively.

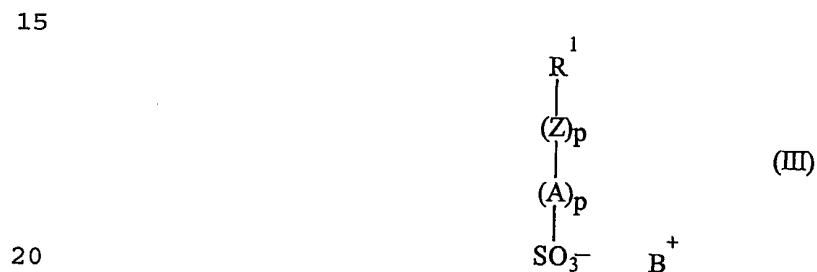
30

There is generally no limitation with respect to how much hydrophobically modified polycarboxylic acid may be

- 9 -

used in this invention other than the amount used results in a dishwashing composition. Typically, however, from about 0.1 to about 10.0, and preferably, from about 0.2 to about 7.0, and most preferably from about 0.3 to about 5.0% by wt. of the dishwashing composition is a hydrophobically modified polycarboxylic acid, based on total weight of the dishwashing composition, including all ranges subsumed therein.

As to the water soluble polymer that reduces phosphate scale formation, such a polymer often comprises at least one structural unit derived from a monomer having the formula:



wherein R^1 is a group comprising at least one sp^2 bond, Z is O, N, P, S, or an amido or ester link, A is a mono- or a polycyclic aromatic group or an aliphatic group and each p is independently 0 or 1 and B^+ is a monovalent cation.

Preferably, R^1 is a C_2 to C_6 alkene (most preferably ethene or propene). When R^1 is ethenyl, Z is preferably amido, A is preferably a divalent butyl group, each p is 1,

- 10 -

and B^+ is Na^+ . Such a monomer is polymerized and sold as Acumer 3100 by Rohm & Haas.

Another preferred embodiment exists when the water
5 soluble polymer is derived from at least one monomer with R^1
as 2-methyl-2-propenyl, Z as oxygen, A as phenylene, each p
as 1 and B^+ as Na^+ , and at least one monomer with R^1 as 2-
methyl-2-propenyl, each p as 0 and B^+ as Na^+ . Such monomers
are polymerized and sold under the name Alcosperse 240 by
10 Alco Chemical.

It is further noted herein that it is within the scope
of this invention for all the polymers used to be a
homopolymer or copolymer, including terpolymers.
15 Furthermore, the polymers of this invention may be
terminated with conventional termination groups resulting
from precursor monomers and/or initiators that are used.

There is generally no limitation with respect to how
20 much water soluble polymer that reduces phosphate scale
formation is used in this invention as long as the amount
used results in a dishwashing composition. Often, from
about 0.5 to about 10.0, and preferably, from about 1.0 to
7.0, and most preferably, from about 1.5 to about 4.5% by
25 weight water soluble polymer is used, based on total weight
of the dishwashing composition, including all ranges
subsumed therein. These water soluble polymers typically
have a weight average molecular weight from about 1,000 to
about 50,000.

30

- 11 -

Phosphate containing builders are a preferred additive in this invention. Such builders typically make up from about 5.0 to about 75.0% by weight of the total weight of the dishwashing composition, including all ranges subsumed therein. Preferably, however, the amount of phosphate containing builder employed is from about 10.0 to about 70.0, and most preferably, from about 15.0 to about 65.0% by weight based on total weight of the dishwashing composition and including all ranges subsumed therein. The phosphate containing builders which may be used in this invention are well known, for example, for binding metals such as Ca and Mg ions, both of which are often abundant in hard water found in dishwashing machines. An illustrative list of the phosphate builders which may be used in this invention include sodium, potassium and ammonium pyrophosphate; alkali metal tripolyphosphates, sodium and potassium orthophosphate and sodium polymetaphosphate, with sodium tripolyphosphate being especially preferred.

Other additives which may be used in this invention include well known items such as perfumes, antifoaming agents, anti-tarnish agents, and processing aids (e.g., polyethylene glycol) which aid in forming tablet-type dishwashing compositions. Such additives, collectively, do not normally make up more than about 8.0% by weight of the total weight of the dishwashing composition.

It is also within the scope of this invention to use conventional dishwashing bleaches and activators (from e.g., from about 0.02 wt. % to about 25.0 wt. %, based on total weight of the dishwashing composition). Such bleaches

- 12 -

include inorganic and organic peracids as well as salts thereof. Examples include epsilon phthalimido perhexanoic acid and Oxone®, respectively.

- 5 Other bleaches which may be used in this invention include hydrogen peroxide and its precursors (e.g., sodium perborate and sodium percarbonate).

If desired, conventional bleach activators (including
10 catalysts) may be used with the bleaches described herein. These activators include N,N,N',N'-tetraacetylenediamine, nonanyloxybenzenesulfonate, cationic nitriles, cholyl (4-sulfophenyl) carbonate, and quaternary imine salts (e.g., N-methyl-3,4-
15 dihydroisoquinolinium p-toluenesulfonate).

Other bleach activators which may be used include transition metal-containing bleach catalysts such as $[\text{Mn}^{\text{IV}}_2(\mu\text{-O})_3(\text{Me}_3\text{TACN})_2](\text{PF}_6)_2$ (as described in U.S. Patent Nos.
20 4,728,455, 5,114,606, 5,153,161, 5,194,416, 5,227,084, 5,244,594, 5,246,612, 5,246,621, 5,256,779, 5,274,147, 5,280,117), $[\text{Fe}^{\text{II}}(\text{MeN}_4\text{py})(\text{MeCN})](\text{ClO}_4)_2$ (as described in EP 0 909 809) and $[\text{Co}^{\text{III}}(\text{NH}_3)_5(\text{OAc})](\text{OAc})_2$ (as described in U.S. Patent No. 5,559,261, WO 96/23859, WO 96/23860, WO
25 96/23861), the disclosures of which are incorporated herein by reference.

It is also within the scope of this invention to employ conventional dishwashing enzymes and buffers. The former
30 typically make up from about 0.5 to about 10.0% by weight of the total weight of the dishwashing composition and include

- 13 -

proteases like Savinase®, Purafect Ox® and Properase® and amylases like Termamyl®, Purastar ST® and Purastar Ox Am®, all of which are commercially available. The latter typically make up from about 5.0 to about 25.0% by weight of the total weight of the dishwashing composition and include well known buffers like sodium disilicate, sodium metasilicate and sodium carbonate.

When washing glassware with the dishwashing composition of this invention, soiled glassware is typically placed in a conventional domestic or commercial dishwashing machine as is the dishwashing composition of this invention (in no particular order). The dishwashing composition, in the form of a liquid, powder or detergent tablet, preferably a tablet, then dissolves in the water of the dishwasher to wash the glassware. The typical dishwashing cycle is from about 10 minutes until about 60 minutes and the typical temperature of the water in the dishwasher is from about 40°C to about 70°C. The glassware resulting from the above-described cleaning method is clean and has an excellent glass appearance (i.e., substantially free of film and spots). Such results are unexpectedly obtained even when hard water at high temperatures (greater than 55°C) is used, in the absence of rinse aid compositions.

25

When marketing the superior dishwashing composition of this invention, it is preferred that the dishwashing composition is formed into a tablet and sold in a package with directions to add the dishwashing composition to the dishwashing machine as a 3-in-1 product. Thus, a dishwasher is charged with the dishwashing composition of this

30

- 14 -

invention without having to add to the dishwasher conventional rinse aid compositions and sodium chloride.

The Examples below are provided to further illustrate an understanding of the present invention, and they are not intended to limit the scope of the invention as set forth in the claims.

Table 1. Abbreviations used in the Examples

AA	Polyacrylic acid
AMPS	2-Acrylamido-2-methylpropane sulfonic acid
DIB	diisobutylene
HEDP	1-hydroxyethylene-1,1-diphosphonic acid
MA	Maleic acid
MMA	Methyl methacrylate
SMS	2-Methyl-2-propene-1-sulfonic acid, sodium salt
SPME	4-[(2-Methyl-2-propenyl)oxy]benzenesulfonic acid, sodium salt

Table 2. Base Formulation used in Examples

Ingredients	% wt
Sodium tripolyphosphate	64.1
Sodium disilicate	20.5
Sodium perborate monohydrate	9.5
Tetraacetyl ethylene diamine - 83 %	2.5
Enzymes*	3.3
1,2,3-Benzotriazole	0.05

* An enzyme mix of protease and amylase, provided by Novo.

- 15 -

All dishwashing machine tests were carried out using a Miele G656 dishwasher setting at the 55°C Normal program, which consisted of a main wash (heated to 55 °C), followed by a cold rinse and a heated (to 65 °C) final rinse with a non-heated drying cycle. Water hardness was adjusted to contain 300 ppm of total hardness ($\text{Ca}^{2+} : \text{Mg}^{2+} = 4:1$, expressed as CaCO_3) and 320 ppm of temporary hardness by addition of sodium bicarbonate (overall expressed as 300/320 ppm water hardness). Typical dishware set used for machine dishwasher tests included the following articles: (1) on the upper rack: 8 clean drinking glasses, 2 lipstick stained drinking glasses 1 Tupperware container and 4 tea stained cups; and (2) on the lower rack: 4 ceramic and 4 stainless steel plates with baked-on egg yolk soil, 4 wheat soiled, 4 potato soiled and 4 Roux Blanc soiled ceramic plates. In addition, 40 grams of ASTM standard food soil, described in Section 5.2 of ASTM Method D 3556-85, "Standard Test Method for Deposition on Glassware During mechanical Dishwashing" was spread on the dishwasher door prior to the beginning of each machine test. This soil consists of 80 % margarine and 20 % low fat powdered milk.

When a cleaning test was ready to be started, 18 g of base formulation (Table 2) was added in the dispenser cup of the dishwasher. In addition, 0.90 g of a hydrophobically modified polycarboxylic acid and 0.54 g of antiscalant were dosed via the dispenser cup or added directly into the machine at the dispenser cup opening in the beginning of the main wash, except for the control run, where no antiscalant was added in the test.

30

- 16 -

The hydrophobically modified (co)polymers used were:

Examples 1-6: Acusol 460, a copolymer of diisobutylene and maleic acid, MW 15,000, supplied by Rohm and Haas Company;

Examples 7-12: Acusol 820, a copolymer of acrylic acid with C_{18} and with $EO_{20}C_{18}$ side chains, MW about 500,000, supplied by Rohm and Haas Company.

10 At the end of a complete machine run, drinking glasses were removed and graded inside a viewing cabinet according to extent of spotting and filming on glasses. Both spotting and filming scores were recorded based on area covered by and intensity of spots and film, respectively. Spotting
15 scores are expressed on a 0 to 4 scale and filming scores are recorded on a 0 to 5 scale, 0 being completely free of spots or film. The sum of spotting and filming score indicates the overall glass appearance, i.e. higher the total score meaning poorer final glass appearance. Results
20 are recorded in Tables 3 and 4.

- 17 -

Examples 1-6

5 **Table 3.** Effect of antiscalant and a hydrophobically modified polymer on glass appearance*

Example	Hydrophobically Modified Polymer ¹	Antiscalant	Glass		Total Score
			Spot	Film	
1 (Control)	MA/DIB	None	3.5	0.4	3.9
2 (Invention)	MA/DIB	AA/MMA/SPME/SMS ²	0.7	1.0	1.7
3 (Invention)	MA/DIB	AA/AMPS ³	0.9	1.0	1.9
4 (Comparative)	MA/DIB	Homopolymer of acrylic acid ⁴	2.4	0.7	3.1
5 (Comparative)	MA/DIB	Mixture of acrylate homopolymer ⁵ and acrylate/maleate copolymer ⁶ (1:2 w/w)	1.7	0.6	2.3
6 (Comparative)	MA/DIB	Mixture of acrylate homopolymer ⁵ and HEDP ⁷ (3:1 w/w)	1.6	0.9	2.5

*Glass appearance is judged by residual film and spots, i.e. higher the total score of spot and film indicating poorer glass appearance.

- 10 1. The hydrophobically modified polymer is Acusol 460, supplied by Rohm and Haas.
2. Alcosperse 240 supplied by Alco Chemical.
3. Acumer 3100 supplied by Rohm and Haas.
4. Acusol 445 supplied by Rohm and Haas.
- 15 5. Sokalan PA25 supplied by BASF.
6. Sokalan CP5 supplied by BASF.
7. Dequest 2016 supplied by Solutia Chemical.

- 18 -

Examples 7-12**Table 4.** Effect of antiscalant and a hydrophobically modified polymer on glass appearance*

5

Example	Hydrophobically Modified Polymer ¹	Antiscalant	Glass		Total Score
			Spot	Film	
7 (Control)	AA with C ₁₈ and EO ₂₀ C ₁₈	None	1.9	1.1	3.0
8 (Invention)	AA with C ₁₈ and EO ₂₀ C ₁₈	AA/MMA/SPME/SMS ²	1.2	0.7	1.9
9 (Invention)	AA with C ₁₈ and EO ₂₀ C ₁₈	AA/AMPS ³	1.1	1.3	2.4
10 (Comparative)	AA with C ₁₈ and EO ₂₀ C ₁₈	Homopolymer of acrylic acid ⁴	1.8	0.9	2.7
11 (Comparative)	AA with C ₁₈ and EO ₂₀ C ₁₈	Mixture of acrylate homopolymer ⁵ and acrylate/maleate copolymer ⁶ (1:2 w/w)	3.2	0.6	3.8
12 (Comparative)	AA with C ₁₈ and EO ₂₀ C ₁₈	Mixture of acrylate homopolymer ⁵ and HEDP ⁷ (3:1 w/w)	2.2	0.8	3.0

*Glass appearance is judged by residual film and spots, i.e. higher the total score of spot and film indicating poorer glass appearance.

- 10 ¹. The hydrophobically modified polymer is Acusol 820, supplied by Rohm and Haas
- ². Alcosperse 240 supplied by Alco Chemical.
- ³. Acumer 3100 supplied by Rohm and Haas.
- ⁴. Acusol 445 supplied by Rohm and Haas.
- 15 ⁵. Sokalan PA25 supplied by BASF.
- ⁶. Sokalan CP5 supplied by BASF.
- ⁷. Dequest 2016 supplied by Solutia Chemical.

As shown in Tables 3 and 4, in the absence of the

20 superior antiscalant of this invention, the hydrophobically modified polycarboxylate in Examples 1 and 7 did not yield

- 19 -

satisfactory glass appearance under hard water washing conditions.

The combination of a hydrophobically modified polycarboxylic acid and a antiscaling polymer containing
5 sulfonated monomeric units greatly and unexpectedly reduces residual spotting and filming on washed glassware, thus giving enhanced glass appearance under hard water washing conditions (Examples 2, 3, 8 and 9).

Conventional dispersing polymers, such as non-modified
10 polycarboxylate polymers, in fact, cause an increase in number of spots on glassware; as such, giving worsened glass appearance (Examples 4, 5, 10 and 11). Inclusion of a diphosphonate de-scaling sequestrant (such as HEDP) does not
15 provide any benefit on enhancing overall glass appearance (Examples 6 and 12).

- 20 -

CLAIMS

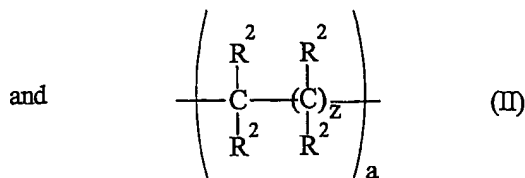
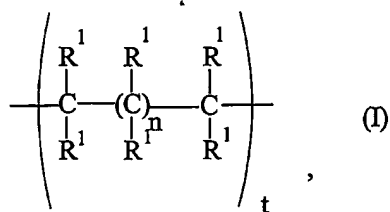
1. A dishwashing composition effective for cleaning glassware in hard water, the dishwashing composition

5 comprising:

- (a) a hydrophobically modified polycarboxylic acid;
and
- (b) a water soluble polymer that reduces phosphate scale formation.

2. The dishwashing composition according to claim 1 wherein the dishwashing composition does not comprise a rinse aid composition.

3. The dishwashing composition according to claim 1 or claim 2 wherein the polycarboxylic acid comprises at least one structural unit selected from the group consisting of:



wherein each R^1 and R^2 are independently a hydrogen, hydroxy, alkoxy, carboxylic acid group, carboxylic acid salt, ester

- 21 -

group, amide group, aryl, C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl or a polyoxyalkylene condensate of an aliphatic group, n is an integer from about 0 to 8, z is an integer from about 1 to about 8, t is an integer from about 0 to about 2,000 and a is an integer from about 0 to about 2,000, with the proviso that a and t are not simultaneously 0 and at least one R¹ or one R² is a carboxylic acid group, or a salt thereof.

4. The dishwashing composition according to claim 3 wherein the hydrophobically modified polycarboxylic acid has $t \geq 1$, $a \geq 1$, and at least one R¹ as a carboxylic acid groups or a salt of a carboxylic acid group, and at least one R² as a C₄₋₂₀ alkyl group or a C₈₋₃₀ ethoxylated condensate of an aliphatic group.

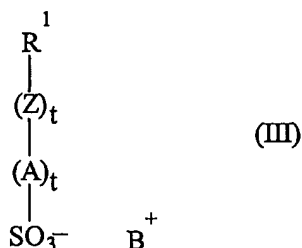
5. The dishwashing composition according to claim 3 wherein the hydrophobically modified polycarboxylic acid has at least two R¹ groups, a carboxylic acid group or salt of a carboxylic acid group, and one R² as a C₅ alkyl group wherein $t \geq 1$ and $a \geq 1$ and a is an integer that is from about 80% to about 120% of t, and $n=0$ and $z=1$.

6. The dishwashing composition according to any preceding claim wherein the dishwashing composition does not require sodium chloride for recharging an ion exchanger.

7. The dishwashing composition according to any preceding claim wherein the water soluble polymer that reduces phosphate scale formation has a polymer backbone comprising

- 22 -

at least one structural unit derived from a monomer having the formula:



wherein R^1 is a group comprising at least one sp^2 bond, Z is O, N, P, S, or an amido or ester link, A is a mono- or a polycyclic aromatic group or an aliphatic group and each t is independently 0 or 1 and B^+ is a monovalent cation.

8. The dishwashing composition according to claim 7 wherein R^1 is ethenyl, Z is amido, A is a divalent butyl group, each t is 1 and B^+ is Na^+ .

9. The dishwashing composition according to claim 7 wherein the polymer backbone has at least one structural unit derived from the monomer wherein R^1 is 2-methyl-2-propenyl, Z is oxygen, A is phenylene, each t is 1 and B^+ is Na^+ , and at least one structural unit derived from the monomer where R^1 is 2-methyl-2-propenyl, each t is 0, and B^+ is Na^+ .

10. The dishwashing composition according to any preceding claim wherein the composition further comprises from about 5.0% to about 75.0% of a phosphate builder.

- 23 -

11. A method for minimising spotting and phosphate scale formation on glassware being cleaned, comprising the steps of:

- 5 (a) charging a dishwashing machine with soiled glassware and a dishwashing composition comprising:
- (i) a hydrophobically modified polycarboxylic acid; and
 - (ii) a water soluble polymer that reduces phosphate scale formation;
- 10 (b) running a dishwashing cleaning cycle; and
- (c) removing clean glassware.

12. The method according to claim 11 wherein a rinse aid composition is not added to the dishwashing composition or
15 the dishwashing machine.

13. The method according to claim 11 or claim 12 wherein an ion exchange salt is not added to the dishwashing machine.

20 14. A kit for a dishwasher comprising a composition comprising:

- (a) a hydrophobically modified polycarboxylic acid;
- (b) a water soluble polymer that reduces phosphate scale formation; and
- 25 (c) instructions which direct a user to utilize the composition in the dishwasher without adding an ion exchange salt or a rinse aid composition, or both.

15 A kit according to claim 13 wherein the kit indicates
30 that the composition is a 3-in-1 composition, or a 3-in-1 detergent, or a 3-in-1 dishwashing composition.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/09274

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D3/37

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	US 6 326 343 B1 (GHATLIA ET AL) 4 December 2001 (2001-12-04) claims	1-15
X	WO 99 58633 A (UNILEVER) 18 November 1999 (1999-11-18)	1,7-10
A	page 18, line 10 - line 20 page 38, line 9 - line 35 page 46; claims	2-6, 11-15
Y	WO 96 00277 A (UNILEVER NV) 4 January 1996 (1996-01-04) page 3, line 24 -page 6, line 31; claims	1-13
Y	WO 98 26036 A (UNILEVER) 18 June 1998 (1998-06-18) page 16, line 17 - line 19; claims	1-13
-/--		



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

11 January 2002

Date of mailing of the international search report

18/01/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Serbetsoglou, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/09274

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 00470 A (PROCTER & GAMBLE) 7 January 1999 (1999-01-07) page 12	1,3-5
A	US 5 958 855 A (BINSTOCK ET AL) 28 September 1999 (1999-09-28) column 5, line 6 -column 6, line 27; claims	1,7-13

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/09274

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6326343	B1	04-12-2001	NONE
WO 9958633	A	18-11-1999	US 6239091 B1 29-05-2001
		AU 8864298 A 16-02-1999	
		AU 9258498 A 29-11-1999	
		BR 9811023 A 19-09-2000	
		BR 9815849 A 30-01-2001	
		WO 9905248 A1 04-02-1999	
		WO 9958633 A1 18-11-1999	
		EP 0998548 A1 10-05-2000	
		EP 1078032 A1 28-02-2001	
		HU 0101860 A2 28-10-2001	
WO 9600277	A	04-01-1996	AU 703378 B2 25-03-1999
		AU 2614795 A 19-01-1996	
		BR 9508089 A 12-08-1997	
		CA 2190349 A1 04-01-1996	
		DE 69511091 D1 02-09-1999	
		DE 69511091 T2 18-11-1999	
		WO 9600277 A1 04-01-1996	
		EP 0766726 A1 09-04-1997	
		ES 2133775 T3 16-09-1999	
		US 5719112 A 17-02-1998	
		ZA 9504521 A 02-12-1996	
WO 9826036	A	18-06-1998	AU 721830 B2 13-07-2000
		AU 5558698 A 03-07-1998	
		BR 9714139 A 29-02-2000	
		WO 9826036 A1 18-06-1998	
		EP 0944703 A1 29-09-1999	
		HU 0000563 A2 28-08-2000	
		ZA 9710550 A 24-05-1999	
WO 9900470	A	07-01-1999	AU 8176198 A 19-01-1999
		EP 0994934 A1 26-04-2000	
		WO 9900470 A1 07-01-1999	
		US 6274539 B1 14-08-2001	
US 5958855	A	28-09-1999	US 6191088 B1 20-02-2001

Form PCT/ISA/210 (patent family annex) (July 1992)

